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Filatov, Michael

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Michael Filatov

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Comment on “Quasirelativistic theory equivalent to fully relativistic theory” [J. Chem. Phys. 123, 241102 (2005)]

Michael Filatov^{a)}

Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

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In a recent publication in this journal,¹ denoted further on as I, Kutzelnigg and Liu described a two-component relativistic theory, which yields the same positive energy (electronic) eigenstates as the exact four-component relativistic theory based on the matrix representation of the Dirac Hamiltonian. In the proposed theory,¹ the non-Hermitian two-component Hamiltonian is defined as [cf. Eq. (20) in I]

$$\mathbf{L} = \mathbf{V} + c\mathbf{X}, \quad (1)$$

where the matrix representation of the operator \tilde{X} , which connects the large and the small components of the four-component relativistic wave function via Eq. (7) in I, is given by [cf. Eq. (23) in I]

$$\mathbf{X} = c^{-1}\mathbf{T} + \frac{1}{4m^2c^2}\mathbf{W}\mathbf{T}^{-1}\mathbf{X} - \frac{1}{2mc^2}\mathbf{X}\mathbf{S}^{-1}\mathbf{L}. \quad (2)$$

In Eqs. (1) and (2), \mathbf{S} , \mathbf{V} , and \mathbf{T} are the usual overlap, potential energy, and kinetic energy matrices, \mathbf{W} is the matrix of the operator $\hat{W} = (\boldsymbol{\sigma} \cdot \mathbf{p})V(\boldsymbol{\sigma} \cdot \mathbf{p})$ ($\boldsymbol{\sigma}$ is the vector of Pauli matrices and \mathbf{p} is the linear momentum operator). Equations (1) and (2) are identical to Eqs. (20) and (23) in I with a minor difference that the original notation \mathbf{U} for the matrix of the operator \hat{W} was replaced with \mathbf{W} .

Equations (1) and (2) comprise a system of coupled equations that is solved by iteration. The system is solved for all electronic states simultaneously. As a check of convergence during the iterations, the energy eigenvalues are obtained from the equation [cf. Eq. (41) in I],

$$\tilde{\mathbf{L}}\mathbf{a}_k = E_k\tilde{\mathbf{S}}\mathbf{a}_k, \quad (3)$$

where the normalization matrix $\tilde{\mathbf{S}}$ is given by [cf. Eq. (40) in I]

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2m}\mathbf{X}^\dagger\mathbf{T}^{-1}\mathbf{X} \quad (4)$$

and the Hermitian Hamiltonian operator $\tilde{\mathbf{L}}$ is given by [cf. Eq. (44) in I]

$$\tilde{\mathbf{L}} = \mathbf{V} + c\mathbf{X}^\dagger + c\mathbf{X} - c^2\mathbf{X}^\dagger\mathbf{T}^{-1}\mathbf{X} + \frac{1}{4m^2}\mathbf{X}^\dagger\mathbf{T}^{-1}\mathbf{W}\mathbf{T}^{-1}\mathbf{X}. \quad (5)$$

The theory described in I represents an interesting development and is capable of yielding the exact solution to the

Dirac equation within the given basis set. Several iterative schemes for solving the respective equations have been suggested and tested.

However, there exists a close connection between the theory developed in I and the methods of elimination of the small component, both in the normalized (NESC) and in the unnormalized (UESC) forms, developed earlier by Dyall.² Although in I some connection between their theory and NESC/UESC was implicitly recognized, it is the purpose of this Comment to spell out this connection explicitly.

In Ref. 2, the operator that connects the large and the pseudolarge components of the four-component wave function is denoted by \mathbf{U} and is connected to \mathbf{X} as

$$\mathbf{U} = c\mathbf{T}^{-1}\mathbf{X}. \quad (6)$$

Substituting (6) in (5) immediately yields the NESC Hamiltonian given in Eqs. (13) and (14) in Ref. 2. Similarly, substituting (6) in (1) yields the UESC Hamiltonian given in Eq. (12) in Ref. 2.

Transforming Eq. (2) with the help of (6) leads to

$$\mathbf{T}\mathbf{U} = \mathbf{T} + \frac{1}{4m^2c^2}\mathbf{W}\mathbf{U} - \frac{1}{2mc^2}\mathbf{T}\mathbf{U}\mathbf{S}^{-1}\mathbf{L} \quad (7)$$

for the matrix \mathbf{U} , using the approach of Kutzelnigg and Liu. This expression seems dissimilar to the formula derived by Dyall for the same operator [cf. Eq. (23) in Ref. 2]. A simple manipulation of Eq. (23) from Ref. 2 using the definition of the Hermitian Hamiltonian operator $\tilde{\mathbf{L}}$ leads to

$$\mathbf{T}\mathbf{U} = \mathbf{T} + \frac{1}{4m^2c^2}\mathbf{W}\mathbf{U} - \frac{1}{2mc^2}\mathbf{T}\mathbf{U}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}}. \quad (8)$$

Equation (8) differs from (7) in the last term. However, as will be shown below, the last terms in (7) and (8) are identical provided that the exact solutions of both equations are obtained.

Let us start from Eq. (21) in Ref. 2 and rewrite it with the help of [cf. Eq. (9) in Ref. 3]

$$\mathbf{A}\mathbf{E}\mathbf{A}^{-1} = \tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}}, \quad (9)$$

where \mathbf{A} denotes the entire set of eigenvectors \mathbf{a}_k and \mathbf{E} is the entire set of eigenvalues E_k of Eq. (3) as

$$\mathbf{U} = \mathbf{T}^{-1}[\tilde{\mathbf{S}}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} - \mathbf{V}]. \quad (10)$$

Equation (10) can easily be transformed to

$$\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} = \mathbf{S}^{-1}\mathbf{L}, \quad (11)$$

which proves the equivalence of Eqs. (7) and (8). Furthermore, with the help of Eqs. (11) and (6) it can be easily shown that the Hermitian eigenvalue problem represented by Eqs. (38)–(41) in I is identical to the NESC equations as given in Eq. (14) of Ref. 2 or in Eqs. (3)–(5) of this work.

Therefore, there exists a close connection between the approach developed in I and the method developed in Ref. 2. This should actually be the case, because all exact quasirelativistic theories must be equivalent to one another. Furthermore, similar to the approach developed in I the expressions

for \mathbf{U} developed in Ref. 2 can be used for iterative construction of exact two-component relativistic Hamiltonian. Equation (11), which is first derived in this Comment, establishes the connection between Hermitian and non-Hermitian formulations of the exact quasirelativistic theory. This equation can also be used for the development of new formulations of the exact quasirelativistic theory.

^{a)}Electronic mail: m.filatov@rug.nl

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